

with  $\text{BrO}_3^-$  at about the same rate. A similar situation was observed in the  $\text{Fe}(\text{CN})_6^{4-}-\text{VO}_2^+$  reaction.<sup>5</sup>

The bromate oxidations of one-electron metal ion reducing agents which have been studied so far appear to fall into mechanistic classifications which depend on the strength of the reducing agent. With the very weak reducing agents  $\text{Ce}(\text{III})^7$  ( $E^\ominus = -1.61 \text{ V}^{23}$ ),  $\text{Mn}(\text{II})^7$  ( $-1.51 \text{ V}^{23}$ ), and  $\text{Np}(\text{V})^{7,8}$  ( $-1.15 \text{ V}^{23}$ ), there is very little direct reduction of  $\text{BrO}_3^-$ . The mechanism involves an autocatalytic production of  $\text{HBrO}_2$  in competition with the disproportionation of  $\text{HBrO}_2$ . The metal ion is oxidized primarily by  $\text{BrO}_2$ . With the somewhat stronger reducing agent  $\text{VO}^{2+}$  ( $-1.00 \text{ V}^{23}$ ), there is a direct reaction of  $\text{VO}^{2+}$  with  $\text{BrO}_3^-$ .<sup>6</sup> However the mechanism is complicated by the fact that the reducing agent is sufficiently weak that  $\text{HBrO}_2$  disproportionation occurs in competition with the  $\text{VO}^{2+}$  reduction of  $\text{HBrO}_2$ . With  $\text{Fe}^{2+}$  ( $-0.77 \text{ V}^{23}$ ), there is a direct reduction of  $\text{BrO}_3^-$  with no apparent complexities.<sup>9</sup> Apparently  $\text{Fe}^{2+}$  is a sufficiently

(23) W. L. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," 2nd ed, Prentice-Hall, New York, N. Y., 1952.

strong reducing agent to reduce  $\text{HBrO}_2$  faster than it can disproportionate, but is not sufficiently strong to reduce  $\text{Br}_2$  fast enough to cause the autocatalysis noted with  $\text{Fe}(\text{CN})_6^{4-}$ . With  $\text{Fe}(\text{CN})_6^{4-}$  ( $-0.69 \text{ V}^{23}$ ) there is a direct reduction of  $\text{BrO}_3^-$  and an autocatalytic reduction due to the  $\text{Fe}(\text{CN})_6^{4-}-\text{Br}_2$  and  $\text{Br}^--\text{BrO}_3^-$  reactions, with a significant portion of the reaction being carried by the autocatalytic path. In this case the reduction of  $\text{HBrO}_2$  is faster than disproportionation but the overall reaction is not sufficiently fast to eliminate the competition between  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Br}^-$  for  $\text{BrO}_3^-$ . It is expected that with stronger reducing agents, the kinetics will be quite straightforward once the reduction of  $\text{BrO}_3^-$  becomes sufficiently fast compared to the  $\text{Br}^--\text{BrO}_3^-$  reaction. Any future entries in this correlation may of course be modified by any peculiarities in the chemical behavior of the metal ion reducing agent.

**Acknowledgment.** Support of this work by the Advanced Research Projects Agency and by the National Science Foundation (Grant GH-33633) is gratefully acknowledged.

**Registry No.**  $\text{Fe}(\text{CN})_6^{4-}$ , 13408-63-4;  $\text{BrO}_3^-$ , 15541-45-4;  $\text{Br}^-$ , 24959-67-9;  $\text{Br}_2$ , 7726-95-6.

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## Mechanism of the Reduction of Uranium(VI) by Titanium(III) and of the Induced Reduction of Vanadium(IV)

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The reduction of uranium(VI) by titanium(III) in acidic chloride or perchlorate media was studied at 25.0° and 0.500 *M* ionic strength. The reaction followed the rate equation  $-d[\text{U}(\text{VI})]/dt = k_1 K_a [\text{Ti}(\text{III})][\text{U}(\text{VI})]/(K_a + [\text{H}^+])$  with  $K_a$  being the acid dissociation constant of  $\text{Ti}^{3+}$ . Values of the parameters were  $k_1 K_a = 13.7 \pm 0.5 \text{ sec}^{-1}$  and  $K_a = 0.0136 \pm 0.0035 \text{ M}$ . The reaction is inhibited by vanadium(IV), according to the rate equation  $-d[\text{U}(\text{VI})]/dt = k_1 k_2 K_a^2 k_3^{-1} [\text{Ti}(\text{III})]^2 [\text{U}(\text{VI})] (K_a + [\text{H}^+])^{-2} / \{ [\text{VO}^{2+}] + k_2 K_a k_3^{-1} [\text{Ti}(\text{II})] (K_a + [\text{H}^+])^{-1} \}$  with  $k_1 k_2 K_a^2 k_3^{-1} = 0.446 \pm 0.014 \text{ M sec}^{-1}$  and  $k_2 K_a k_3^{-1} = 0.0324 \pm 0.0011 \text{ M}$ . The inhibition is interpreted in terms of a competition for U(VI) between V(IV) and Ti(III), which is verified by the observed production of V(III).

### Introduction

As part of a series of kinetic studies of oxidations by  $d^0$  metal oxy ions such as  $\text{Cr}(\text{VI})$ ,<sup>2-4</sup>  $\text{V}(\text{V})$ ,<sup>5-7</sup> and  $\text{Mn}(\text{VII})$ , to determine the kinetic consequences of the substitution inertness of the reducing agent, we have now studied the reduction of U(VI) by the labile reductant<sup>8</sup> Ti(III). It has been possible to elucidate the mechanism of this reaction in considerable detail by studying the inhibition of the reaction by  $\text{VO}^{2+}$ . The oxidation of  $\text{Ti}^{3+}$ , which has been studied in only a few cases,<sup>7</sup> has now been extended to the entire series of  $d^0$  metal ion oxidants— $\text{VO}_2^+$ ,<sup>7</sup>  $\text{HCrO}_4^-$ ,<sup>4</sup>  $\text{MnO}_4^-$ ,<sup>9</sup> and

$\text{UO}_2^{2+}$ —making it possible to examine the common features of all these reactions to determine those factors which affect the mechanistic behavior of  $\text{Ti}^{3+}$ .

### Experimental Section

Solutions of uranium(VI) were prepared by dissolving weighed amounts of Alfa Inorganics  $\text{UO}_3$  in a known excess of  $\text{HClO}_4$ . The solutions were analyzed by reducing U(VI) to U(IV) with zinc amalgam under  $\text{N}_2$  and titrating aliquots in 1 *M*  $\text{H}_2\text{SO}_4$  with 0.1 *M* Ce(IV) to a blue ferroin end point at 50°. The reduced uranium solution was shaken well with air before titration to oxidize any U(III) to U(IV). Results agreed well with the weight of  $\text{UO}_3$  taken. Acid concentration was obtained by difference. All other materials were prepared and analyzed as described earlier.<sup>5,7</sup> The handling of solutions and the procedures for kinetic measurements have been described.<sup>7</sup> The acid concentrations in the two reactant solutions to be mixed in the stopped-flow apparatus were controlled appropriately to suppress dissociation of the Ti(III) dimer.<sup>7</sup> Data were obtained principally at 648 nm, a wavelength of maximum absorbance for  $\text{U}^{2+}$ , but no difference in results was noted upon variation of the wavelength over the small ranges in which reasonable absorbance changes could be obtained. First-order plots of  $\ln(D_\infty - D_t)$  vs. time ( $D =$  absorbance) were generally linear to  $\geq 90\%$  reaction under pseudo-first-order conditions. With the slower reactions, infinity readings were sometimes in doubt, due to diffusion of reactants into the observation

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(1) Taken in part from the Ph.D. thesis of T. P. L., University of Pennsylvania, 1972.

(2) J. P. Birk, *J. Amer. Chem. Soc.*, **91**, 3189 (1969).

(3) J. P. Birk and J. W. Gasiewski, *Inorg. Chem.*, **10**, 1586 (1971).

(4) J. W. Gasiewski and J. P. Birk, unpublished experiments.

(5) J. P. Birk, *Inorg. Chem.*, **9**, 125 (1970).

(6) J. P. Birk and S. V. Weaver, *Inorg. Chem.*, **11**, 95 (1972).

(7) J. P. Birk and T. P. Logan, *Inorg. Chem.*, **12**, 580 (1973).

(8) A. M. Chmelick and D. Fiat, cited in D. J. Hewkins and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1970).

(9) T. P. Logan and J. P. Birk, unpublished experiments.

cuvette at long times, so the Guggenheim method<sup>10</sup> was then used. Where checks could be made, excellent agreement was obtained between the two types of plots.

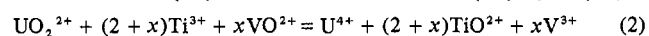
## Results

**Stoichiometry.** The expected reaction between Ti(III) and U(VI) is given by



with equilibrium constant  $K = 6 \times 10^7$  at 25° calculated from the oxidation potentials,<sup>11</sup> so the reaction should go essentially to completion. This stoichiometry was confirmed by a spectrophotometric titration which gave a value of  $[\text{Ti}^{3+}]/[\text{UO}_2^{2+}] = 2.00 \pm 0.01$ . The product spectrum in the 650-nm region where U(IV) is the principal absorbing species agrees well with that of a mixture of  $\text{U}^{4+}$  and  $\text{UOH}^{3+}$ , the difference between calculated<sup>12</sup> and observed absorbances being  $\leq 4\%$ .

In the presence of  $\text{VO}^{2+}$ , the stoichiometry is changed by virtue of the U(VI)-induced reduction of V(IV) by Ti(III)



The value of  $x$  is determined by the relative concentrations of Ti(III) and V(IV) and the ratio of rate constants for reaction of these species with U(VI), as explained below. The products of a mixture initially containing  $8.20 \times 10^{-3} M$  Ti(III),  $5.00 \times 10^{-3} M$  U(VI),  $2.97 \times 10^{-3} M$  V(IV), and  $0.292 M$   $\text{H}^+$  gave an absorbance of 0.38 at 648 nm, while a mixture containing no V(IV) but otherwise identical gave an absorbance of 0.45. Values calculated for the above stoichiometry, based on  $1.45 \times 10^{-3} M$   $\text{V}^{3+}$  being produced in the first experiment, are 0.39<sub>6</sub> and 0.47, in good agreement with the respective observed values.

**Kinetics of the U(VI)-Ti(III) Reaction.** When the dimer dissociation is properly suppressed,<sup>7</sup> the U(VI)-Ti(III) reaction (eq 1) exhibits only a single absorbance change, with no evidence for a faster step as observed in the V(V)-Ti(III)<sup>7</sup> and Cr(VI)-Ti(III)<sup>4</sup> reactions. The kinetics of this step were determined at 0.500  $M$  ionic strength (maintained with LiCl and  $\text{LiClO}_4$ ) and 25.0° over the concentration ranges (8–50)  $\times 10^{-4} M$  Ti(III), (4–25)  $\times 10^{-5} M$  U(VI), 0.0434–0.300  $M$   $\text{H}^+$ , and 0.050–0.300  $M$   $\text{Cl}^-$ . Good pseudo-first-order kinetics were always observed. With 0.050  $M$   $\text{H}^+$  and  $1.50 \times 10^{-3} M$  Ti(III), the observed rate constant was independent of the  $\text{Cl}^-$  concentration, varying by only  $\pm 1\%$  over the range 0.050–0.300  $M$ . At each  $[\text{H}^+]$ , data followed the rate equation

$$-d[\text{UO}_2^{2+}]/dt = k_0[\text{UO}_2^{2+}] = k_{\text{ox}}[\text{UO}_2^{2+}][\text{Ti(III)}] \quad (3)$$

Conformance to this equation is shown by the data in Table I. The  $[\text{H}^+]$  dependence of  $k_{\text{ox}}$  follows the equation

$$k_{\text{ox}} = a/(b + [\text{H}^+]) \quad (4)$$

Values of  $k_{\text{ox}}$  were fit to eq 4 with a nonlinear least-squares computer program<sup>13</sup> with each point weighted as  $k_{\text{ox}}^{-2}$ , giving  $a = 13.7 \pm 0.5 \text{ sec}^{-1}$  and  $b = 0.0136 \pm 0.0035 M (=K_a$  of  $\text{Ti}^{3+})$ . Conformance of the data to eq 4 is shown by Figure 1.

A check was made for the possibility of a dependence of the rate on the products of the reaction. When  $\text{TiO}^{2+}$  (and  $\text{VO}^{2+}$ ) was generated by the Ti(III)-V(V) reaction and added

Table I. Rate Constants for the U(VI)-Ti(III) Reaction at 0.500  $M$  Ionic Strength and 25.0°

$[\text{H}^+]$ , $M$	$10^4 \times$ $[\text{Ti(III)}]$ , $M$	$k_0$ , $\text{sec}^{-1}$		$k_{\text{ox}}$ , $M^{-1} \text{sec}^{-1}$	
		Obsd <sup>a</sup>	Calcd <sup>b</sup>	Obsd <sup>a</sup>	Calcd <sup>b</sup>
0.050	8.21	0.176	0.177	2.14	
0.050	9.95	0.206	0.214	2.07	
0.050	15.0	0.329	0.323	2.20	
0.050	17.2	0.379	0.371	2.20	
				Av 2.15 $\pm$ 0.05	2.15
0.100	8.21	0.100	0.0990	1.22	
0.100	10.0	0.122	0.121	1.22	
0.100	12.0	0.133	0.145	1.11	
0.100	15.0	0.192	0.181	1.28	
0.100	16.0	0.183	0.193	1.14	
0.100	18.0	0.203	0.216	1.13	
0.100	20.0	0.239	0.241	1.19	
0.100	25.0	0.322	0.302	1.29	
0.100	30.0	0.369	0.361	1.23	
0.100	34.5	0.428	0.416	1.24	
				Av 1.21 $\pm$ 0.05	1.21
0.300	30.0	0.125	0.131	0.417	
0.300	40.0	0.178	0.175	0.445	
0.300	50.0	0.211	0.218	0.422	
				Av 0.428 $\pm$ 0.011	0.437
0.0434	15.0	0.355	0.360	2.37	2.40
0.070	15.0	0.254	0.246	1.70	1.64
0.090	15.0	0.220	0.198	1.47	1.32
0.120	15.0	0.158	0.154	1.05	1.03
0.140	15.0	0.146	0.134	0.975	0.895
0.150	15.0	0.128	0.125	0.854	0.834
0.200	15.0	0.0990	0.0961	0.661	0.642
0.250	15.0	0.0779	0.0779	0.520	0.520

<sup>a</sup> Defined in eq 3. <sup>b</sup> Calculated from eq 3 and 4 and the parameters given in the text.

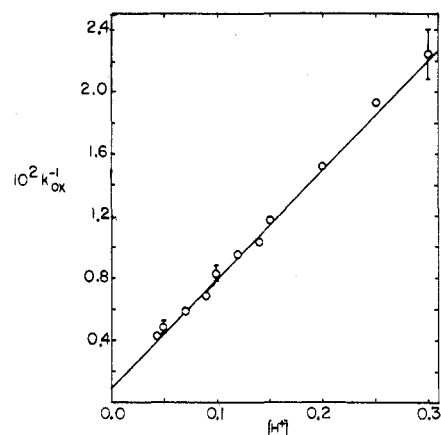


Figure 1. Plot of  $k_{\text{ox}}^{-1}$  vs.  $[\text{H}^+]$  showing conformance to eq 4. The line was calculated from eq 4 and the parameters given in the text.

to the U(VI) solution, the reaction slowed down compared to the same conditions but with no added  $\text{TiO}^{2+}$ . However, when  $\text{TiO}^{2+}$  was generated by the Ti(III)-U(VI) reaction, no change in rate was observed. Since  $\text{U}^{4+}$  is also generated in this case, a product dependence with terms of the form  $[\text{U}^{4+}]/[\text{TiO}^{2+}]$  would be consistent with these observations since this ratio remains constant throughout the reaction, but no other product dependence would be allowed. The reaction was shown to be independent of both  $[\text{TiO}^{2+}]$  and  $[\text{U}^{4+}]$  by experiments in which  $\text{VO}^{2+}$  was added as  $\text{VO}(\text{ClO}_4)_2$ . The rate was identical with that in the experiment with  $\text{VO}^{2+}$  and  $\text{TiO}^{2+}$  in the same amounts formed from the Ti(III)-V(V) reaction, indicating that the inhibition was due to  $\text{VO}^{2+}$ .

**Kinetics of the Inhibition by  $\text{VO}^{2+}$ .** The inhibiting effect of  $\text{VO}^{2+}$  was investigated under the same conditions as the

(10) E. A. Guggenheim, *Phil. Mag.*, [7] 2, 538 (1926).

(11) W. M. Latimer, "Oxidation Potentials", 2nd ed, Prentice-Hall, New York, N. Y., 1952.

(12) K. A. Krause and F. Nelson, *J. Amer. Chem. Soc.*, 72, 390 (1950).

(13) The programs used were based on reports from Los Alamos Scientific Laboratory (LA-2367 + addenda) and were modified to operate on the IBM 360/75 computer.

simple Ti(III)-U(VI) reaction, with  $\text{VO}_2^{2+}$  added to the  $\text{UO}_2^{2+}$  solution prior to mixing with the  $\text{Ti}^{3+}$  solution in the stopped-flow apparatus. The inhibition placed the reaction in the uncomfortable range of rates which are somewhat too high for conventional measurements but are near the long-time stability limit of the stopped-flow apparatus due to diffusion of reactants into the observation cuvette. In addition, at long times the absorbance increase was followed by an absorbance decrease due to the slow direct reaction between  $\text{Ti}^{3+}$  and  $\text{VO}_2^{2+}$ . For these reasons, the Guggenheim method<sup>10</sup> was used with fairly small time constants and the first 50% of reaction was weighted heavily in the pseudo-first-order plots. Rate constants evaluated in this manner appear to be quite accurate since variation of the Guggenheim time constant had no effect and extrapolation of the resulting data to  $[\text{VO}_2^{2+}] = 0$  yielded the correct results.

Data determined for the  $\text{VO}_2^{2+}$  inhibition are given in Table II. At constant  $[\text{H}^+]$  and  $[\text{Ti(III)}]$ , the variation of  $k_0 = -d \ln [\text{UO}_2^{2+}]/dt$  with  $[\text{VO}_2^{2+}]$  is given by

$$k_0 = c/(d + [\text{VO}_2^{2+}]) \quad (5)$$

Conformance to this equation is shown by a plot of  $k_0^{-1}$  vs.  $[\text{VO}_2^{2+}]$  in Figure 2. The accessible range of  $[\text{H}^+]$  was limited at the lower end by the acidity of the Ti(III) stock solutions and at the upper end by the onset of the Ti(III)-V(IV) reaction at long times. However, as shown in Table III, even though the range of  $[\text{H}^+]$  is rather narrow, the acid dependences of the parameters  $c$  and  $d$  can be established with reasonable certainty from the slopes and intercepts of plots of  $k_0^{-1}$  vs.  $[\text{VO}_2^{2+}]$  as  $c = e(K_a + [\text{H}^+])^{-2}$  and  $d = f(K_a + [\text{H}^+])^{-1}$  where  $K_a = 0.0136 \pm 0.0035 M$  is taken as the parameter  $b$  in eq 4. This yields the equation to describe the  $[\text{VO}_2^{2+}]$  and  $[\text{H}^+]$  dependences

$$k_0 = e(K_a + [\text{H}^+])^{-2} / \{f(K_a + [\text{H}^+])^{-1} + [\text{VO}_2^{2+}]\} \quad (6)$$

Consideration of data at constant  $[\text{H}^+]$  and  $[\text{VO}_2^{2+}]$  with  $[\text{Ti(III)}]$  being varied as in Table II indicates a  $[\text{Ti(III)}]$  dependence between first- and second-order which decreases with increasing concentration, suggesting  $e = g[\text{Ti(III)}]^2$  and  $f = h[\text{Ti(III)}]$ . This is confirmed by reasonably good linearity of a plot of  $[\text{Ti(III)}]k_0^{-1}$  vs.  $[\text{Ti(III)}]^{-1}$  as shown in Figure 3. This gives as a final equation for the dependence of  $k_0$  on all species

$$k_0 = g[\text{Ti(III)}]^2(K_a + [\text{H}^+])^{-2} / \{h[\text{Ti(III)}](K_a + [\text{H}^+])^{-1} + [\text{VO}_2^{2+}]\} \quad (7)$$

All data from Tables I and II were simultaneously fit to this equation, using a nonlinear least-squares computer program.<sup>13</sup> The resultant values of the parameters are  $g = 0.446 \pm 0.014 M \text{ sec}^{-1}$ ,  $h = 0.0324 \pm 0.0011 M$ , and  $K_a = b = 0.0136 \pm 0.0035 M$ . Conformance of data to eq 7 is shown by a plot of a rearrangement of this equation given in Figure 4. The data extrapolate properly to  $[\text{VO}_2^{2+}] = 0.0$  to give  $g/h = 13.8 \text{ sec}^{-1}$  in excellent agreement with the value of  $a = 13.7 \text{ sec}^{-1}$ .

## Discussion

The rate equation for the reduction of U(VI) by Ti(III) (eq 1) indicates that the first electron-transfer step is rate determining. The acid dependence is consistent with the acid dissociation of  $\text{Ti}^{3+}$  with  $K_a = 0.0136 M$ . This value is in excellent agreement with that determined spectrophotometrically<sup>14</sup> (0.012 or 0.015  $M$ , depending on the activity coefficients used<sup>15</sup>). Values of  $K_a$  extracted from kinetic data for the Ti(III)-V(V) (0.04  $M$ )<sup>7</sup> and the Ti(III)-Cr(VI)

**Table II.** Rate Constants for the  $\text{VO}_2^{2+}$  Inhibition of the Ti(III)-U(VI) Reaction at 25.0° and 0.500  $M$  Ionic Strength

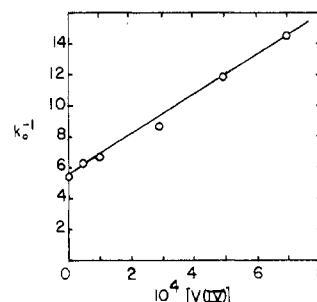
$[\text{H}^+]$ $M$	$10^4[\text{Ti(III)}]$ , $M$	$10^4[\text{V(IV)}]$ , $M$	$k_0$ , $\text{sec}^{-1}$	
			Obsd <sup>b</sup>	Calcd <sup>c</sup>
0.050	15.0	0.993	0.309	0.288
0.050	15.0	1.16	0.304	0.283
0.050	15.0	2.95	0.257	0.236
0.050	15.0	4.97	0.189	0.199
0.050	15.0	6.99	0.180	0.172
0.050	15.0	9.00	0.160	0.151
0.100	15.0	0.497	0.158	0.163
0.100	15.0	0.993	0.149	0.152
0.100	15.0	2.95	0.116	0.107
0.100	15.0	4.97	0.0849	0.0841
0.100	10.0	5.00	0.0447	0.0442
0.100	15.0	5.00	0.0871	0.0838
0.100	20.0	5.00	0.119	0.130
0.100	25.0	5.00	0.173	0.179
0.100	32.9	5.00	0.284	0.261
0.100	15.0	6.98	0.0693	0.0690
0.100	20.0	0.993	0.188	0.207
0.100	20.0	2.95	0.152	0.160
0.200	15.0	0.497	0.0821	0.0793
0.200	15.0	0.993	0.0673	0.0673
0.200	15.0	2.95	0.0394	0.0422

<sup>a</sup>  $[\text{Ti(III)}]_0 \geq 20[\text{U(VI)}]_0$ . <sup>b</sup>  $k_0 = -d \ln [\text{UO}_2^{2+}]/dt$ . <sup>c</sup> Calculated from eq 7 and the parameters given in the text.

**Table III.** Acid Dependence of the Parameters  $c$  and  $d$  from Eq 5<sup>a</sup>

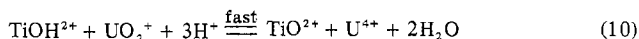
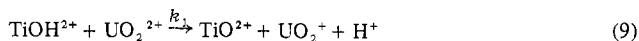
$[\text{H}^+]$ $M$	$10^4 c$ , $M \text{ sec}^{-1}$	$10^6 c(K_a + [\text{H}^+])^2$ , $M^3 \text{ sec}^{-1}$	$10^4 d$ , $M$	$10^4 d(K_a + [\text{H}^+])$ , $M^2$
0.050	2.56	1.03	7.17	0.455
0.100	0.746	0.962	3.73	0.423
0.200	0.213	0.971	2.13	0.455
		Av 0.988 ± 0.028		Av 0.444 ± 0.014

<sup>a</sup>  $[\text{Ti(III)}] = 1.50 \times 10^{-3} M$ ;  $K_a = b = 0.0136 \pm 0.0035 M$  (eq 4).



**Figure 2.** Plot of  $k_0^{-1}$  vs.  $[\text{V(IV)}]$  showing conformance of the V(IV) dependence to eq 5 ( $[\text{Ti(III)}] = 1.50 \times 10^{-3} M$ ,  $[\text{H}^+] = 0.100 M$ ). The line was calculated from eq 7 and the parameters given in the text.

(0.03  $M$ )<sup>4</sup> reactions are not in as good agreement, but this probably reflects the difficulty of extracting information from multistep absorbance changes in those cases. The rate equation suggests  $\text{TiOH}^{2+}$  as the active Ti(III) species, in agreement with the results of most other studies of Ti(III) reductions<sup>16</sup>



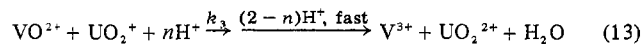
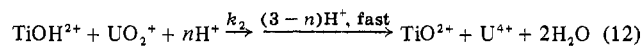
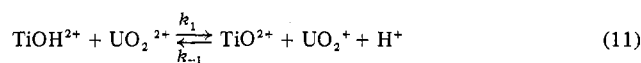
(15) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions", 3rd ed, Reinhold, New York, N. Y., 1958, pp 638, 752.

(16) See ref 7 and references given therein.

(14) R. L. Pecsok and A. N. Fletcher, *Inorg. Chem.*, 1, 155 (1962).

with  $k_{\text{ox}} = k_1 K_a / (K_a + [\text{H}^+])$  so  $K_a = 0.0136 M$  and  $k_1 = 1.01 \times 10^3 M^{-1} \text{sec}^{-1}$ . A possible two-electron transfer in the rate-determining step is consistent with this rate equation as well but is ruled out by the rate equation for inhibition by  $\text{VO}^{2+}$  and by the unfavorable requirement of the existence of  $\text{Ti(V)}$  in such a mechanism. Competitive removal of  $\text{UO}_2^{2+}$  by disproportionation of this species can be eliminated since deviations from first-order behavior would be expected.<sup>17</sup> The correct kinetics would be observed if disproportionation, but not eq 10, was important, but the shortest half-life for disproportionation of  $\text{UO}_2^{2+}$  under the conditions of this study is about 7000 sec,<sup>18</sup> while the redox reaction had half-lives on the order of 2 sec.

The inhibition by  $\text{VO}^{2+}$  is interpreted essentially as a U(VI)-induced reduction of  $\text{VO}^{2+}$  by  $\text{Ti(III)}$ , due to reaction of  $\text{VO}^{2+}$  with  $\text{UO}_2^{2+}$ , which has been observed to occur rapidly.<sup>19</sup> The net overall reaction is then given by eq 2. The direct reduction of  $\text{VO}^{2+}$  by  $\text{Ti(III)}$  under conditions comparable to this study has half-lives of several hundred seconds,<sup>20</sup> about 2 orders of magnitude slower than the overall induced reaction. The mechanism proposed involves eq 8 followed by



If  $\text{UO}_2^{2+}$  is treated as a steady-state intermediate, the rate equation is

$$-d[\text{UO}_2^{2+}]/dt = k_1 k_2 K_a^2 [\text{Ti(III)}]^2 [\text{UO}_2^{2+}] (K_a + [\text{H}^+])^{-2} / \{k_{-1} [\text{TiO}^{2+}] [\text{H}^+]^{1-n} + k_2 K_a [\text{Ti(III)}] (K_a + [\text{H}^+])^{-1} + k_3 [\text{VO}^{2+}]\} \quad (14)$$

If the  $k_{-1}$  term is small compared to the other denominator terms, this equation reduces to the form of the observed rate equation (eq 7), with  $g = k_1 k_2 K_a^2 k_3^{-1}$  and  $h = k_2 K_a k_3^{-1}$ , giving  $k_1 = 1.01 \times 10^3 M^{-1} \text{sec}^{-1}$  and  $k_2/k_3 = 2.38$ . The value of  $n$  in eq 12-14 cannot be determined but must be the same in each case, since the  $[\text{H}^+]^n$  term cancels in the rate equation. Further support for this assignment of mechanism is given by agreement between observed and calculated absorbances in the experiments described under the stoichiometry section. The relative rates of eq 12 and 13 are given by  $(d[\text{U(IV)}]/dt)/(d[\text{V(III)}]/dt) = d[\text{U(IV)}]/d[\text{V(III)}] = k_2 [\text{Ti(III)}]/k_3 [\text{V(IV)}]$  which can be solved as a linear first-order differential equation to give  $[\text{V(III)}]_{\infty} = \{([\text{V(III)}]_0 - 2k_2/k_3 [\text{V(III)}]_0) (1 - 2k_2/k_3)^{-1}\} + \{([\text{Ti(III)}]_0 - [\text{V(IV)}]_0) (1 - 2k_2/k_3)^{-1}\} [1 - [\text{V(III)}]_{\infty} / [\text{V(IV)}]_0]^{2k_2/k_3}$ . Solution of this equation by successive approximations ultimately leads to a correct value of the absorbance of the product mixture, as described earlier.

Values can be estimated for each of the rate constants in the mechanism, eq 11-13. A value for the equilibrium constant for the sum of eq 8 and 11 can be obtained from oxidation potentials<sup>11</sup> as  $0.14 M^2 = k_1 K_a / k_{-1}$ . With  $k_1 K_a = 13.8 \text{sec}^{-1}$ , the value  $k_{-1} = 99 M^{-2} \text{sec}^{-1}$  is obtained. An estimate for  $k_3$  can be obtained from the results of Newton and Baker,<sup>19</sup> who determined a value of  $k_3 [\text{H}^+]^n = 1400 M^{-1}$

(17) T. W. Newton, *J. Phys. Chem.*, **62**, 943 (1958).

(18) G. Gordon and H. Taube, *J. Inorg. Nucl. Chem.*, **16**, 272 (1961).

(19) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **69**, 176 (1965).

(20) J. P. Birk, unpublished experiments, A. G. Sykes, private communication.

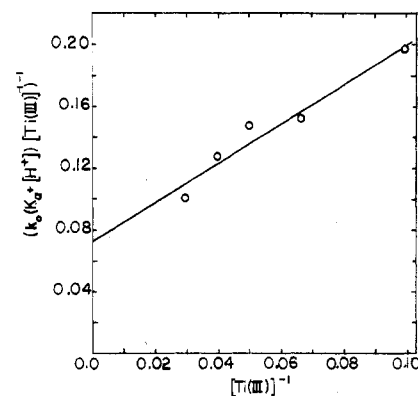


Figure 3. Plot of  $[k_0(K_a + [\text{H}^+])[\text{Ti(III)}]^{-1}]$  vs.  $[\text{Ti(III)}]^{-1}$  showing conformance of the  $\text{Ti(III)}$  dependence to eq 7 ( $[\text{VO}^{2+}] = 5.00 \times 10^{-4} M$ ,  $[\text{H}^+] = 0.100 M$ ). The line was calculated from eq 7 and the parameters given in the text.

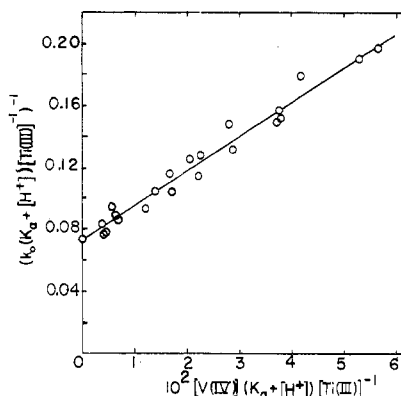


Figure 4. Plot of  $(k_0(K_a + [\text{H}^+])[\text{Ti(III)}]^{-1})$  vs.  $[\text{V(IV)}](K_a + [\text{H}^+])[\text{Ti(III)}]^{-1}$ , showing conformance of all data to eq 7. The line was calculated from eq 7 and the parameters given in the text.

$\text{sec}^{-1}$  at  $25^\circ$ ,  $1.00 M \text{HClO}_4$ , and  $I = 2.00 M$ . A value of  $k_3$  at  $I = 0.50 M$  can be predicted by means of an extended Debye-Huckel equation,  $\log k_3 = \log k_3^0 + \alpha \Delta Z^2 I^{1/2} (1 + D I^{1/2})^{-1} + EI$ , with  $\alpha = 0.5091$  at  $25^\circ$ . Newton and Baker<sup>19</sup> suggested a value of  $E = 0.1 M^{-1}$  and we have used this value in the calculation. The value of  $\Delta Z^2$  is uncertain since it is not known how many protons are consumed in the rate-determining step of eq 13. We have considered two situations:  $n = 0$ ,  $\Delta Z^2 = 4$ ;  $n = 1$ ,  $\Delta Z^2 = 10$ . Intuitively, the latter values seem more likely since overall  $\text{H}^+$  is consumed in this reaction and it is common in such cases to consume some of the  $\text{H}^+$  at or prior to the rate-determining step. The term  $D$  is composed of a constant ( $0.3286 \times 10^8$  at  $25^\circ$ ) multiplied by the distance of closest approach of the species forming the activated complex. This distance was estimated from ionic crystalline radii,<sup>21</sup> assuming the configuration  $\{\text{O-U-O-O-V}\}^\ddagger$  for the activated complex, giving  $D = 2.30$ . A check on this approach was made on the  $\text{U(IV)-V(II)}$  reaction,<sup>19</sup> where we calculate  $D = 2.65$  and the empirically determined value was 2.74. This results in values for  $k_3$  at  $I = 0.50 M$  of  $470 M^{-2} \text{sec}^{-1}$  if  $n = 1$ ,  $\Delta Z^2 = 10$  and  $730 M^{-1} \text{sec}^{-1}$  if  $n = 0$ ,  $\Delta Z^2 = 4$ . Then from  $k_2/k_3 = 2.38$ ,  $k_2 = 1.12 \times 10^3 M^{-2} \text{sec}^{-1}$  ( $n = 1$ ) or  $k_2 = 1.74 \times 10^3 M^{-1} \text{sec}^{-1}$  ( $n = 0$ ).

Estimated values of these rate constants can be used to test the assumption that the  $k_{-1}$  term in eq 14 is indeed negligible. Under the least favorable conditions this term contributes less than 5% to the denominator of eq 14, and in most experiments with added  $\text{VO}^{2+}$ , it contributes less than

(21) S. S. Batsanov, *Zh. Strukt. Khim.*, **3**, 596 (1962).

3%, so within the experimental error this term would go unnoticed.

The mechanism proposed for the first step in the Ti(III)-V(V) reaction<sup>7</sup> involves the formation of a binuclear complex  $\text{TiOHVO}_2^{3+}$  from  $\text{TiOH}^{2+}$  and  $\text{VO}_2^+$ , with formation constant  $5700 M^{-1}$ . Under similar conditions, a binuclear species  $\text{TiOHCrO}_4$  is proposed in the Ti(III)-Cr(VI) reaction,<sup>4</sup> with formation constant  $\sim 10^{10} M^{-1}$ . In the present study of the Ti(III)-U(VI) reaction, attempts to observe an absorbance change corresponding to binuclear complex formation or to observe a term in the redox rate equation resulting from complex formation were unsuccessful. If it is assumed that a species  $\text{TiOHUO}_2^{4+}$  is formed in small amounts, an estimate of the formation constant is  $< 10 M^{-1}$  based on the limitations of experimental error. A very distinct two-step reaction is observed in the Ti(III)-Mn(VII) reaction,<sup>9</sup> with the first step presumably corresponding to formation of a binuclear complex such as  $\text{TiOHMnO}_4^+$ . We do not yet have sufficiently quantitative data to assign a value to the formation constant in this system, but preliminary indications are that it will be quite large, probably consistent with the trend in values established with the other  $d^0$  metal ions. It would appear that the value of the formation constant is in large part determined by the charges on the species involved.

The presence of  $\text{TiOH}^{2+}$  as the reactive species in each of these systems as well as most of those studied previously may be indicative of an inner-sphere mechanism. Arguments have been developed in the reduction of cobalt(III) complexes for an inner-sphere mechanism when the hydroxy complex has a high reactivity compared to the aquo complex,<sup>22</sup> but whether this increase in reactivity is due to the electron-mediating effect of bridging  $\text{OH}^-$  or to a stability imparted to the inner-sphere complex by the  $\text{OH}^-$  ligand is still open to question.<sup>23</sup>

(22) O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, **91**, 1968 (1969).

(23) M. P. Litelpe and J. F. Endicott, *Inorg. Chem.*, **10**, 1420 (1971).

The Ti(III) systems differ in that the  $\text{OH}^-$  ligand is originally bound to the reducing agent, but we have shown that for some  $\text{Cr(VI)}^2$  and  $\text{V(V)}^{5,6}$  oxidations, donation of the bridging ligand by the reducing agent is possible. While the general high reactivity of  $\text{TiOH}^{2+}$  in the  $d^0$  metal ion systems may be indicative of an inner-sphere mechanism, an argument which is supported but not proved by the formation of binuclear complexes, it would be difficult to extend such arguments to other oxidants, especially those which are substitution inert and do not expand their coordination sphere upon reduction. An alternate reason for the presence of  $\text{TiOH}^{2+}$  is that in the process of oxidation,  $\text{Ti}^{3+}$  loses two protons to form  $\text{TiO}^{2+}$ . It is not unusual for one or more protons to be lost in or before the rate-determining step when protons are lost on going from reactants to products, presumably due to lowering of the energy barrier when the transition state more closely resembles the products.

In each of the Ti(III) reductions we have examined, no dependence on the  $\text{Cl}^-$  concentration was noted over wide ranges. Unless  $\text{Cl}^-$  were to play some specific role, such as that of a bridging ligand, it would be surprising to see a  $[\text{Cl}^-]$  dependence, since Ti(III) exists only to a small extent as  $\text{TiCl}^{2+}$ .<sup>24</sup> In those cases where a  $[\text{Cl}^-]$  dependence was noted,<sup>16</sup> the oxidizing agents have a marked tendency to form  $\text{Cl}^-$  complexes, which are probably responsible for this effect.

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**Registry No.**  $\text{Ti}^{3+}$ , 22541-75-9;  $\text{UO}_2^{2+}$ , 16637-16-4;  $\text{VO}^{2+}$ , 20644-97-7.

(24) H. J. Gardner, *Aust. J. Chem.*, **20**, 2357 (1967).

## Notes

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### Mechanism of the Bromate Ion Oxidation of Aquoiron(II)

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The bromate ion oxidation of ferrous ion has been studied as part of a series of oxy anion oxidations of intermediate strength reducing agents such as the cyanide,<sup>1</sup> bipyridyl, and mixed-ligand complexes of iron(II). This reaction is also of interest in relation to the metal ion catalyzed oscillating reaction between bromate ion and malonic acid.<sup>2-4</sup> It has

been reported that Fe(III) will cause oscillating behavior in this system.<sup>5</sup> This seemed rather surprising in light of recent mechanistic interpretations of these oscillating reactions.<sup>3,4,6</sup> A crucial part of this mechanism is the appropriate pathway for oxidation of the metal ion by  $\text{BrO}_3^-$ , which is followed only by very weak metal ion reducing agents (e.g.,  $\text{Ce}^{3+}$ ,<sup>7</sup>  $\text{Mn}^{2+}$ ,<sup>7</sup>  $\text{NpO}_2^{+}$ <sup>7,8</sup>). We have verified the occurrence of oscillating behavior in the  $\text{BrO}_3^-$ -malonic acid reaction catalyzed by a number of metal ion-diimine complexes with oxidation potentials less than -1.1 V but were unable to observe any oscillations with  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  as the catalyst, in agreement with predictions based on the proposed mechanism.<sup>3,4,6</sup> The kinetics of the  $\text{Fe}^{2+}$ - $\text{BrO}_3^-$  reaction reported here are also inconsistent with  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  giving rise to oscillating behavior.

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(6) R. M. Noyes, R. J. Field, and R. C. Thompson, *J. Amer. Chem. Soc.*, **93**, 7315 (1971).

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(3) R. M. Noyes, R. J. Field, and E. Koros, *J. Amer. Chem. Soc.*, **94**, 1394 (1972).